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Report No. ARF-C6001-2
(Progress Report)

PREPARATION AND EVALUATION OF NEW HYDRAULIC FLUIDS

Bureau of Ships
Washington 25, D. C.

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

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6 PREPARATION ~~AND~~ EVALUATION OF NEW HYDRAULIC FLUIDS

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The purpose of this project is to develop new fire-resistant hydraulic fluids based on fluorinated sulfur-containing compounds. The compounds will be synthesized specifically to meet the critical property requirements. Various derivatives of sulfur hexafluoride and other fluorinated materials will be investigated.

The electrolytic fluorination of di-n-propyl sulfide, $(C_3H_7)_2S$, is now being studied in an attempt to prepare the perfluoro derivative:

$$(C_3H_7)_2S \xrightarrow[\text{electrolysis}]{\text{HF}} (C_3F_7)_2SF_4 \qquad (1)$$

Hoffman and his coworkers (ref. 1) have prepared this compound. The reaction shown in Equation 1 has been carried out and the products are now being analyzed. The Simon's cell shown in Figures 1 and 2 was used. The di-n-propyl sulfide was placed in the cell and the cell was closed. The hydrogen fluoride was condensed into the metering reservoir, measured, and transferred into the cell. Although the cell itself was not refrigerated, the reflux condenser was cooled with dry ice. After the reaction was complete, the products were removed.

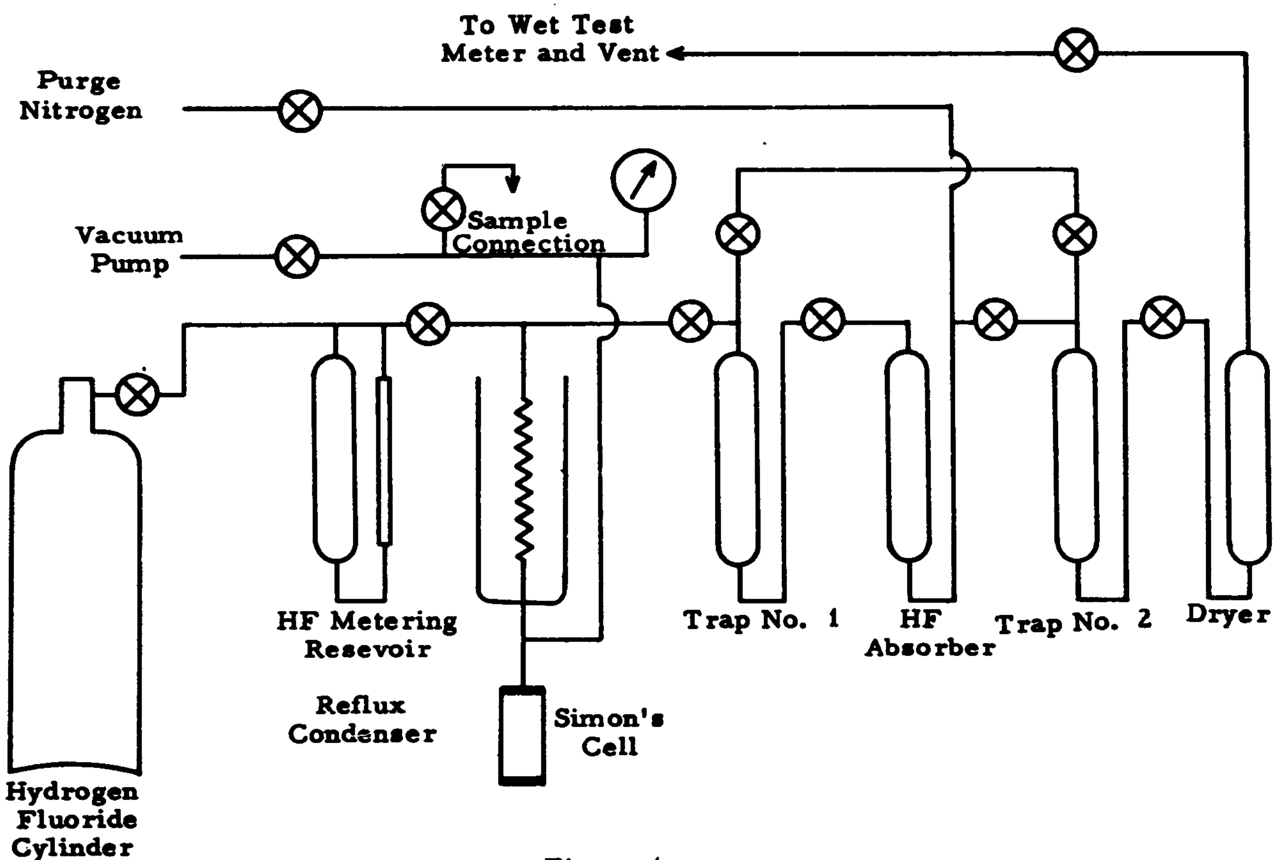


Figure 1

ELECTROLYTIC FLUORINATION APPARATUS

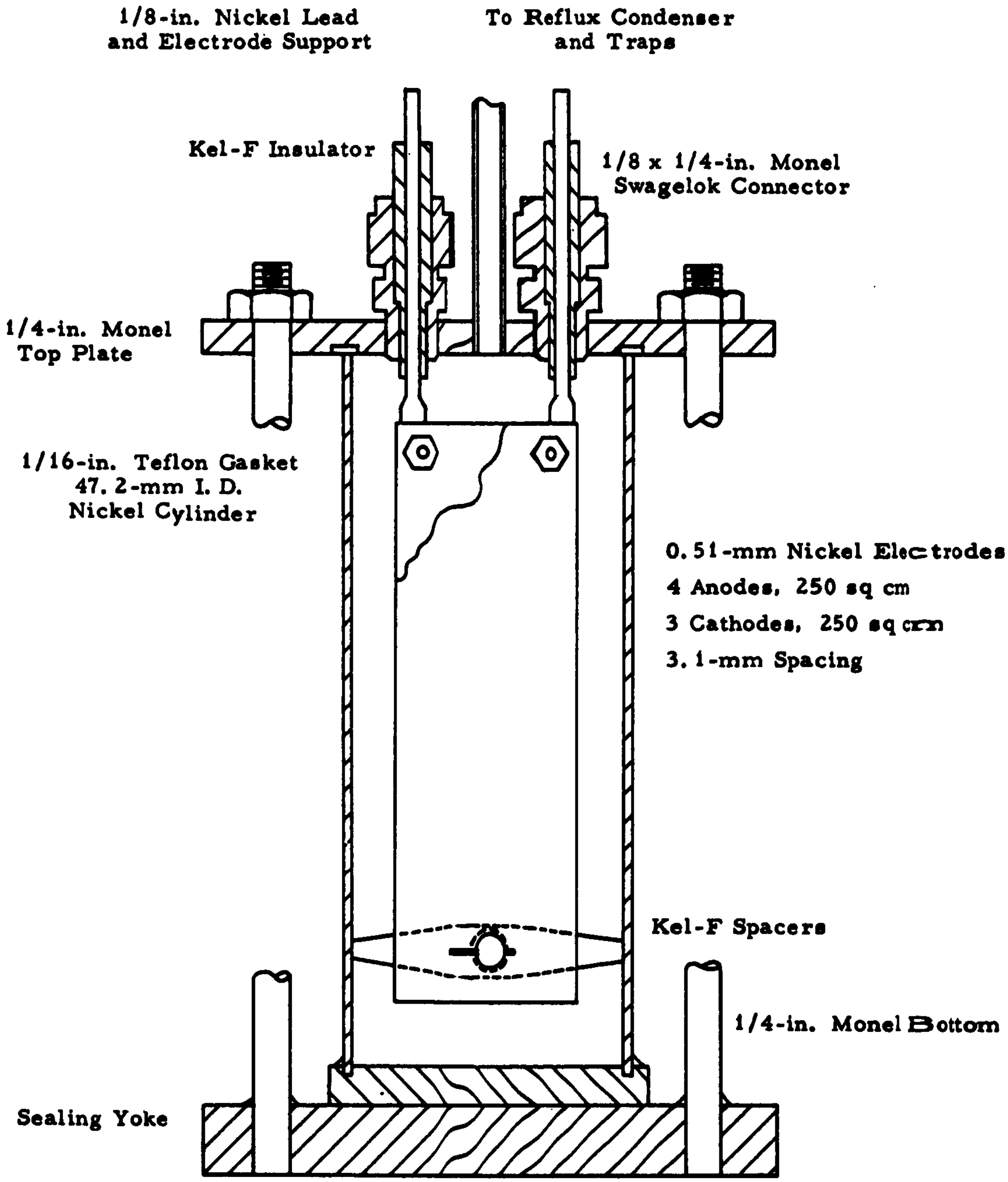
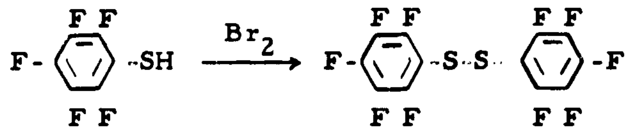


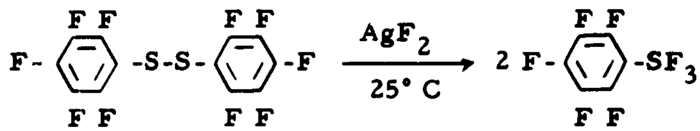
Figure 2

SIMON'S CELL

The preparation of pentafluorosulfur pentafluoride, $C_6F_5SF_5$, is being carried out as shown in Equations 2 through 4.



(2)



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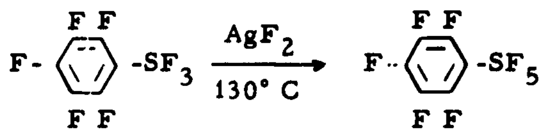

(4)

About 100 g of product was obtained by means of the reaction shown in Equation 2. The fluorination of the disulfide, Equation 3, resulted in a colorless liquid which is now being characterized.

The viscosities of a number of fluorocarbons have been checked to determine the structural characteristics necessary for the desired viscosity index (Table 1). Generally, the viscosity and the viscosity index are of the same order of magnitude for hydrocarbons of the same skeleton. However, the absolute viscosities of the fluorocarbons for which data are available are higher than those of saturated hydrocarbons having the same structure. For example, n-C_7H_{16} has a viscosity of 3.397 millipoises at 38.34° C, while n-C_7F_{16} has a viscosity of 7.33 millipoises at 38.2° C. If the viscosities are expressed as kinematic viscosity, the ratio of absolute viscosity to density, the fluorocarbons will probably have lower values

Table 1

VISCOSITIES OF SOME FLUOROCARBONS[a]

Fluorocarbon	Viscosity at Temp., millipoises	Temp., °C
n-Heptforane	13.67	0.42
	8.61	27.5
	8.05	32.1
	7.33	38.2
	6.64	45.0
C_9F_{16}(saturated)	2.19 [b]	18
	1.39 [b]	37.8
1,3,5-Trimethforylcyclohexforane	37.49	0.28
	17.27	35.7
	11.25	62.2
	7.32	94.6
Naphthalforane	53.39	24.6
	11.61	99.3
Anthracforane	22.4	99.5
Tetraisobutforane	32	99.5
Chrysforane ($C_{18}F_{30}$)	60	99.5
Retforane ($C_{18}F_{32}$)	60	99.5

[a] Simons, J. H., "Fluorine Chemistry", Academic Press, Inc., New York, Vol. I, p. 439, 1950.

[b] Viscosity is given in centistokes.

than the corresponding hydrocarbons. This is a consequence of the greater density of the fluorocarbons.

The temperature coefficients of viscosity of n-heptforane and 1, 3, 5-trimethforylcyclohexforane are greater than those of the corresponding hydrocarbons (ref. 2). This is probably true of most fluorocarbons.

Fluorocarbon oils have been used as lubricants, and the results of tests on properties related to this use have been reported (ref. 3-7). Tests made on various fluorocarbon oils showed that they were good lubricants, comparable in this respect to good hydrocarbon lubricants (ref. 3). This is also true of stabilized polymers of $CF_2=CFCl$ (ref. 8).

Early qualitative data indicated that the carbon skeleton structure has less effect on the viscosity of a fluorocarbon oil than the corresponding structure does in the case of a hydrocarbon oil. Fluorocarbon oils made by the catalytic fluorination process, even when prepared from hydrocarbon oils of markedly different composition, showed about the same viscosity (ref. 3). It is expected that fluorocarbons in the lubricating oil range should have a boiling point range of 150 to 200°C at a pressure of 10 mm Hg.

Data on the vapor pressure of low-molecular-weight fluorocarbons (Table 2) indicate that the Trouton constant, ΔS_v, is normal for these materials.

Table 2

VAPOR PRESSURE DATA
FOR SOME LOW-MOLECULAR-WEIGHT FLUOROCARBONS[a]

Fluorocarbon	ΔH_v at B. P., cal/mole	ΔS_v, e. u. /mole	B. P., °C
CF_4	2947	20.3	-128
C_2F_6	3860	19.8	-76.3
n-C_5F_{12}	6510	21.5	29.32
iso-C_5F_{12}	6490	21.4	30.12
cyclo-C_5F_{10}	6300	21.3	22.48

[a]Based on data given in: Simons, J. H., "Fluorine Chemistry," Academic Press, Inc., New York, Vol. I, p. 436, 1950.

The list of fluorocarbons in Table 3 shows how some of the physical properties vary with structure.

During February all the data in Tables 1, 2, and 3 will be analyzed to determine the effect of structure on viscosity index. Also, the products obtained from reaction 1 through 4 will be characterized.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION
of Illinois Institute of Technology

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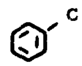
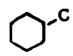
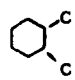
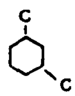
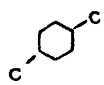
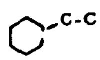
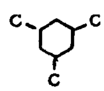
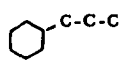
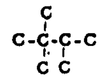
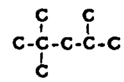
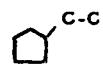
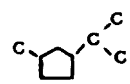
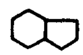
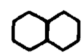
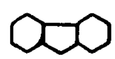
Table 3

PHYSICAL PROPERTIES OF SOME FLUOROCARBONS[a]

Fluorocarbon	Carbon Structure	B. P., °C	Density, g/cc
C_6F_6		81.0-82.0	1.612 (25°C)
C_7F_8		103.5	1.660 (25°C)
C_6F_{12}		-[b]	-[c]
C_7F_{14}		76.32	1.7994 (20°C)
C_8F_{16}		102.61	1.8672 (20°C)
C_8F_{16}		102.12	1.8560 (20°C)
C_8F_{16}		100.97	1.8503 (20°C)
C_8F_{16}		97-98	1.295 (20°C)
C_9F_{18}		125.18	1.9025 (20°C)
C_9F_{18}		117-117.5	1.291 (20°C)
C_6F_{14}	C-C-C-C-C-C	55.9-56.7	1.253 (26°C)
C_7F_{16}	C-C-C-C-C-C-C	82.43	1.7332 (20°C)
C_7F_{16}		82	1.7535 (30°C)
C_8F_{18}		104	1.8002 (30°C)
C_5F_8		33-35	
C_5F_{10}		22.48	1.648 (20°C)
C_6F_{12}		47.1	1.268 (20°C)
C_7F_{14}		75.05	1.7707(20°C)
C_9F_{18}		114-117	1.292 (20°C)
C_9F_{16}		117.83	1.3077 (20°C)
$C_{10}F_{18}$		140	1.3118 (20°C)
$C_{13}F_{22}$		190	1.3264 (20°C)

[a]Based on data given in: Simons, J. H., "Fluorine Chemistry", Academic Press, Inc., New York, Vol. I, pp. 452-458, 1950.

[b]Sublimes at 760 mm, 51° C.

[c]Solid.

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